OIPE SEP 1 2 2002 JC180 PATENT & TRADEMARK OFFICE

PATENT
Docket No. 146712000400

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#18 9/18/02

In the application of: Qixu (David) CHEN et al.	Examiner: K. Bernatz
Serial No.: 09/559,347	Group Art Unit: 1773
Filing Date: April 27, 2000	
For: MEDIUM WITH NiNb SEALING LAYER	

RECEIVED
SEP 16 2002
TC 1700 MAIL ROOM

DECLARATION OF PROFESSOR CAROLINE ROSS UNDER 37 CFR 1.132

Commissioner for Patents
Washington, D.C. 20231

Sir:

Caroline Ross declares under penalty of perjury under the laws of the United States of America as follows:

1. I received a Ph.D. from Cambridge University, UK, in 1988. After working at Harvard University for two years as a postdoctoral researcher, I joined Komag, Inc. in 1991 as a Research Engineer. I worked there until 1997, when I joined Massachusetts Institute of Technology (MIT) as a faculty member. I am now a tenured Associate Professor at MIT. My research is directed towards the magnetic properties of thin films and small structures, particularly for data storage applications. At this time I oversee the research activities of 6 graduate students and 2 post-doctoral researchers. I study magnetic materials used in a variety of applications, such as recording media and heads, magneto-optical devices, and sensors. I also study the fabrication of magnetic films and small structures using sputtering, pulsed laser deposition, evaporation and electrodeposition combined with nanolithography and self-assembly

methods, and measuring and modeling the magnetic behavior of the resulting films and nanostructures. Examples include arrays of small magnetic 'dots' for patterned recording media, magnetoresistive elements for magnetic random access memories, magnetooptical materials for optical components, and thin films for hard disk media. I also oversee a Thin Film Laboratory which includes a pulsed laser deposition system and a UHV sputter system.

2. While I was at Komag, I worked on several projects related to hard disk recording media, including the process described in U.S. Patent 5,980,997 for laser-texturing a substrate coated with a NiNb layer. I also worked on several other laser texturing processes described in U.S. Patents 6,143,375, 6,103,404 and 5,741,560, and in a publication, "A method for laser zone texturing of glass based magnetic media using Nd:YAG lasers," Proc. Materials Research Society vol. 517 p. 427 (1998) [Attachment A]. I am very familiar with the art relating to magnetic recording media.

3. This declaration explains that the use of NiNb as a "sealing layer," i.e. a diffusion barrier to cover Li-containing substrates, as proposed by Applicants of the pending application, is not obvious based on the prior art of Ross (U.S. Patent 5,980,997) combined with that of Taguchi (U.S. Patent 5,874,376). To recapitulate, Ross shows that NiNb is suitable in a laser texturing process, while Taguchi discloses the use of a Li-containing substrate.

4. I am using the term "sealing layer" as defined in the specification of the pending application, as follows:

> A sealing layer or a sealing means is a layer that can reduce Li concentration on the surface of the magnetic media to less than 500 counts/minute by the time-of-flight secondary ion mass spectroscopy (TOF-SIMS) method as follows. After the disc media are sputter-deposited, about 15Å of lubricant was applied onto the surfaces of the discs. The discs were sent into a chamber in the environment of 60°C and 80% relative humidity (RH) for 4 days, then were analyzed with TOF-SIMS. The surface concentration of lithium is used as disc corrosion criteria and is expressed in μg/disc or counts/minute.

5. Ross does not contain any reference or experimental measurement of the properties of NiNb as a diffusion barrier, which is the technological application discussed by Applicants. The purpose of the NiNb layer in the Applicants' disclosure is to prevent the diffusion of Li ions from a Li-containing substrate through the sputtered films and onto the top surface of the disk. The NiNb layer is therefore acting as a diffusion barrier (or "sealing layer" in the specification's terminology). This is a distinctly different purpose from that described in Ross. In Ross, the purpose of the NiNb is to produce an appropriately bumpy surface when irradiated with a laser pulse. The bumps are useful to prevent the head from sticking to the disk, and are formed over a limited area of the substrate. There is no reason to believe that a material that works well for laser texture should work well as a sealing layer, since these two applications rely on different physical properties of the thin film materials. For instance, in Ross Fig. 9, curve 82 shows that a magnetic alloy of $CoNiPtTaTiSiO_2$ (100nm thick) on a 25 nm Cr underlayer can form bumps when irradiated with a laser. Yet in the Applicants' disclosure, a 63 nm thick carbon/CoCrPtTa/CrMo stack was found to be inadequate for preventing the diffusion of Li to the surface, as discussed in the following paragraph. The $CoNiPtTaTiSiO_2$ and CoCrPtTa are broadly similar alloys, both containing a majority of Co. We can therefore see that a Co-alloy apparently works well for laser texture but poorly as a Li diffusion barrier. In contrast, based on hindsight gained from Ross and the pending application, I now realize that NiNb unexpectedly works well as both a laser texture layer and as a diffusion barrier. While I was investigating laser texturing layers, I tried a wide range of materials including NiNb of different compositions, Cu, Al, Ta, hydrogenated carbon, NiAl, Ni_3P, $CoNiPtTaTiSiO_2$, and stacks such as Cr/Al/Cr and Ti/AlTi, all with thicknesses in the range of 40–1000 nm. I found no particular relation between the structure or chemical composition of the film, and its response to the laser pulses. Even today, the response of materials to laser pulses is not well understood and so cannot easily be predicted. There is therefore no way to predict how well a material will work as a diffusion barrier based on its performance as a laser texture layer. Thus, based on the information given in

Ross relating to NiNb as a laser texture layer, it would not have been obvious to one skilled in the art that NiNb should also perform well as a diffusion barrier.

6. From the Applicants' data [Attachment B] on Li diffusion through a NiNb/CrMo/CoCrPtTa/C stack, it is clear that the NiNb is the active material in the diffusion barrier, while the CrMo/CoCrPtTa/C has little effect on diffusion. The CrMo/CoCrPtTa/C stack is 63 nm thick, and allows 2700 counts/min of Li to diffuse to the top of the film stack under the experimental methods used here. However, the insertion of only 5 nm of NiNb is sufficient to reduce the Li concentration at the top of the film stack by a factor of 3, which means that 5nm NiNb is significantly better at preventing Li diffusion than the 63 nm CrMo/CoCrPtTa/C stack. 10 nm NiNb reduces the Li concentration by a further factor of 3. 20 nm NiNb reduces the Li concentration to an undetectable level. Thus, comparing their performance as diffusion barriers, even a thin NiNb layer of 5-10 nm thickness is far superior to a CrMo/CoCrPtTa/C stack of 63 nm thickness.

7. We now address the issue of the desirable NiNb film thickness. Ross showed that bumps of various sizes and shapes could be formed in films of NiNb when exposed to a laser pulse (the process is called laser texturing). The data in Ross were taken from samples consisting of a substrate coated with 25 nm Cr then X nm NiNb, where X is greater than or equal to 100nm. The data shows that as the laser power increases, the bumps formed become taller, but at sufficiently high laser powers, the film can burn through which is undesirable. If the NiNb is thinner, it burns through more easily (i.e. at lower laser power), as seen in Fig. 8 of Ross. The data in Fig. 8 shows that 100 nm thick NiNb burns through at 0.4–3.2 μJ per pulse, depending on the pulse time and laser spot size. There is no data presented for any film thickness below 100 nm NiNb. However, one would expect, based on the data presented in Fig. 8, that for film thicknesses below about 50 nm, the burn-through thresholds will be quite low, and it is not clear that such films will be suitable for the laser-texturing application, because of the difficulty in controlling very low-power laser pulses. Thus, the data in Ross would teach against the use of

very thin NiNb films for laser texturing because of the low burn-through thresholds. From Ross, one might gain the impression that laser texturing a thin NiNb layer could result in burn-through or deep holes and other damage to the NiNb layer, such that it would not have prevented migration of Li from the substrate to the magnetic layer. So a person of ordinary skill in this art would not have been motivated to select a 45 nm or less thick NiNb layer directly on a glass substrate.

8. Regarding the function of the Cr underlayer in Ross, the examples given of NiNb laser texture layers also include a 25 nm Cr underlayer to enhance adhesion between the NiNb and the glass substrate. Figures 8 and 9 of Ross refer to NiNb films deposited over a Cr underlayer. However, the Cr layer is not indispensable to the laser texture process if a substantially thick NiNb film of a thickness greater than 100 nm is deposited directly onto glass substrates. In Attachment A, data are presented based on 130 nm thick NiNb deposited directly onto glass substrates, and good results were obtained for the laser texture process. As explained in paragraph 5, it is totally unpredictable as to whether laser texturing a thin NiNb layer of 45 nm or less would necessarily have allowed the NiNb layer to act as the claimed "sealing layer."

9. In conclusion, Ross and the Applicants' disclosure describe two very different technological advances. In Ross, NiNb is chosen because of its convenience as a laser texture layer and because it forms bumps with suitable and well-controlled shapes when irradiated with a laser. Its diffusion barrier properties are not considered or discussed and, therefore, would not have been obvious to a person of ordinary skill based on the disclosure of Ross. In the Applicants' disclosure, NiNb acts as a diffusion barrier for preventing Li migration from a Li-containing substrate. Even today, it is not obvious that a material that responds well to laser texturing should also be a good diffusion barrier, much less would it have been obvious at the time of the claimed invention. Moreover, the process of laser texturing, in which the NiNb layer is exposed to a laser beam, may adversely affect the diffusion barrier properties of the layer. I have observed, from experiments on films of various materials, that laser irradiation can burn

through, crack or otherwise weaken the film. Such damage would severely degrade the ability of the film to prevent the diffusion of Li, and it is particularly likely to occur in thinner films such as those described in the pending application. In particular, it is not necessary that a NiNb film of 450Å (45 nm) or less, or indeed of any material in this thickness range, subjected to laser texturing, would prevent diffusion of Li, due to the unknown relationship between diffusion-barrier properties and bump formation in materials, and the unpredictable effects of laser texturing on the diffusion-barrier properties of thin films. Thus the diffusion-barrier property of NiNb layer would not have been recognized by a person of ordinary skill who would have combined the teachings of Ross and Taguchi and thereby sputtered NiNb directly onto a Li-containing substrate. Without even recognizing that a NiNb layer sputtered directly on a Li-containing substrate could prevent Li migration, I fail to understand how a person of ordinary skill could have arrived at this invention by combining the teachings of Ross and Taguchi.

I declare under penalty of perjury under the laws of the United States that the foregoing is true and correct. Executed at Cambridge, Massachusetts, United Stated of America, this 21st day of August, 2002.

Caroline Ross

ATTACHMENT A.

MRS 517 (1998) p427

A METHOD FOR LASER ZONE TEXTURING OF GLASS BASED MAGNETIC MEDIA USING Nd:YAG LASERS

M. P. Rosenblum *, C. A. Ross **
* Komag Inc., 1704 Automation Parkway, San Jose, CA 95131
** Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02139

ABSTRACT

Laser zone texturing of nickel-plated, aluminum based magnetic media has become a preferred method of providing a precisely controlled head landing zone. The Nd:YAG lasers used for this process are not suitable for directly texturing glass substrates. A novel method has been developed which allows the use of the existing Nd:YAG laser systems to zone texture glass based magnetic media.

An amorphous sputtered film of a non-magnetic Ni alloy provides a texturing layer which absorbs the laser pulse and controllably forms regular, small protrusions. Optimization of the alloy composition results in small cone-shaped bumps. Laser power sensitivity exhibits a region of invariance for a range of film thickness. This behavior provides a wide margin for manufacture by reducing the effect of thickness variation on laser bump height.

Disks fabricated using this form of laser zone texture exhibit excellent tribology performance. TEM images show the Ni alloy to be amorphous and featureless. The sputtered film does not influence the properties of the subsequently sputter deposited isotropic magnetic films.

INTRODUCTION

In a magnetic hard disk drive during normal operation the read/write transducer, or head, flies above the rotating disk on an air bearing. The head, which is mounted on a suspension connected to an actuator, moves radially across the disk to locate one of a group of concentric recording tracks.

In the start-up and shut-down processes of the disk drive, the head comes into contact with the disk. When the rotation speed is below the level necessary to create an air bearing with sufficient stiffness, the head will slide along the surface of the disk. If the two contacting surfaces of the disk and head are smooth, a large frictional force will develop. In addition, once the head remains, for a period of time, in stationary contact with the disk, a significant static friction, or stiction, force may arise.

To reduce friction and stiction to acceptable levels in a disk drive, one solution is to controllably roughen, that is texture, the surface of the disk [1]. Initially, mechanical texturing using an abrasive was applied across the entire disk surface. Eventually, the requirements for a smoother surface at high recording densities caused the texturing to be limited to a restricted area or zone at the inner diameter of the disk. The head is restricted to land and take-off from within this zone.

Within the past several years, a new method for zone texturing hard disk media has become widely used [2, 3]. The technique, known as laser zone texturing, produces an array of

consistent "bumps" in a precisely controlled location on the Ni-P plated aluminum substrate. The most common lasers in production use are high-repetition-rate Q-switched infrared lasers (Nd:YAG, Nd:YLF or Nd:YVO_4). These lasers provide stable pulses at high repetition rates. The results are production systems with good process control and high throughput.

These infrared lasers (λ = 1064 nm) are not suitable for direct use with glass or glass-ceramic substrates. A novel method was developed which allows the use of existing laser systems with alternate substrates such as glass and glass-ceramic. A sputtered film that coats the surface of the substrate provides a texturing layer that absorbs the laser pulse and controllably forms regular, small bumps. Disks fabricated using this form of zone texture exhibit low friction and stiction values, even after many tens of thousands of continuous start-stop (CSS) cycles.

EXPERIMENT

Alloys of nickel and niobium were chosen for investigation because they form non-magnetic amorphous films over a broad composition range when sputter deposited [4]. In addition, the amorphous films have reported glass transition temperatures above 400°C, which make them suitable for the subsequent sputtering of magnetic films at elevated process temperatures.

Films are deposited by dc magnetron sputtering onto polished alumino-silicate or boro-silicate glass substrates. The cathode power is kept constant at a level that results in a deposition rate of 40 Å per second. Thickness is controlled by sputter time. The argon gas pressure is 6.5 mTorr. (0.86 Pa).

Texturing is performed using Nd:YVO_4 lasers with pulse widths of 14 ns or 65 ns and spot sizes of 11 µm and 10 µm, respectively. Bump heights are measured using an optical interferometer microscope, MicroXam, manufactured by Phase Shift Inc.

The measurement of bump height as a function of laser power and its associated slope, the bump height sensitivity, is made by texturing individual tracks of bumps, each at a fixed laser power.

Continuous start-stop (CSS) testing is performed by configuring a spindle, a head and suspension assembly with a strain-gauge. The test sequence is to spin-up to operating speed, in this case 7200 rpm, maintain this speed for a short period, about 2 seconds, and then spin-down to a complete stop. The cycle is then repeated. For each cycle, the maximum static or dynamic friction is determined. The CSS graph is the plot of the maximum value for each cycle.

The time at which the head remains in static contact with the disk surface is a few seconds. However, at every 5,000th cycle (or at least four times during the test) the time of static contact is increased to 2 hours to assess the static friction after an extended parking duration.

RESULTS

When irradiated with suitable laser pulses, thin films of Ni-Nb on glass produce reproducible and uniform bumps. The shape of the bump is primarily conical. This compares with the crater (or ridge) and sombrero shapes that are formed on plated NiP/Al substrates. Cross-sections from optical interferometric imaging of the three shapes are shown in Figure 1.

The bump on Ni-Nb/glass does not conserve volume unlike the crater and sombrero bumps on NiP/Al. There may be some contribution to the bump height from the glass substrate

as a result of indirect heating. Laser bumps formed directly on glass using CO_2 laser pulses are also conical in shape and do not conserve volume [5]. The chemical resistance of the film prevented its selective etching (i.e., without also etching the glass substrate).

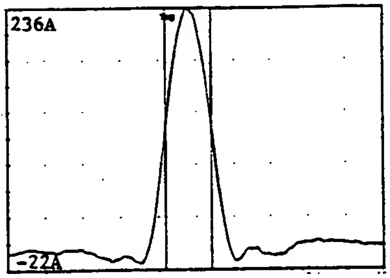

Figure 1a. Laser bump on $Ni_{50}Nb_{50}$ on glass. Peak height 236Å. FWHM 4.25 µm

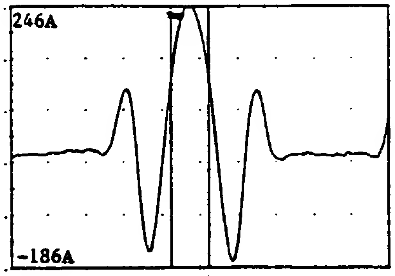

Figure 1b. Laser bump on NiP/Al. 14 ns pulse. Peak height 246Å. FWHM 3.5 µm

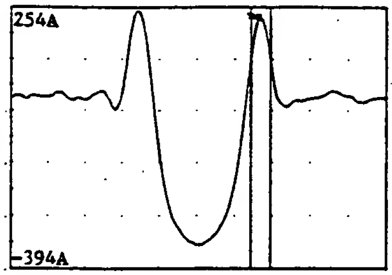

Figure 1c. Laser bump on NiP/Al. 65 ns pulse. Peak height 254Å. FWHM 1.9 µm

Bump heights for a 1300 Å film of $Ni_{50}Nb_{50}$ as a function of normalized laser pulse energy for pulse widths of 14 ns and 65 ns are shown in Figures 2 and 3, respectively.

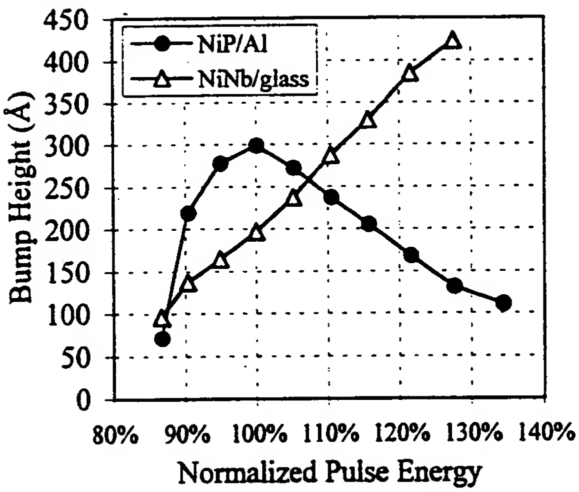

Figure 2. Power series for polished plated NiP/aluminum disk and 1300Å $Ni_{50}Nb_{50}$ on a glass disk. <u>Laser pulse width is 14 ns</u>. Spot size is 11 µm. 100% pulse energies are 1.34µJ and 0.67µJ for the NiP/Al and $Ni_{50}Nb_{50}$, respectively.

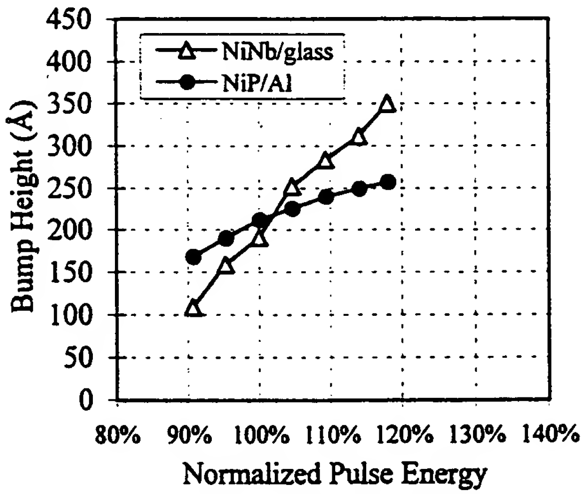

Figure 3. Power series for polished plated NiP/aluminum disk and 1300Å $Ni_{50}Nb_{50}$ on a glass disk. <u>Laser pulse width is 65 ns</u>. Spot size is 10 µm. 100% pulse energies are 1.2µJ and 0.96µJ for the NiP/Al and $Ni_{50}Nb_{50}$, respectively.

Bump heights for plated NiP/Al are shown for comparison. The shapes of the bumps on Ni-Nb are conical for both conditions, whereas the bumps on NiP/Al are sombrero shape for 14 ns pulses and crater shape at 65 ns. Formation of a central peak feature in Ni-Nb may result from forces other than chemicapillary, which has been proposed [6] for NiP/Al.

For practical application, the bump height sensitivity to laser power should be small enough so that fluctuations in the laser pulse energy do not result in unacceptable bump height

variation. In order to maintain an acceptable manufacturing tolerance, the bump height sensitivity should have a weak dependence on film thickness.

Both of these criteria are met with a $Ni_{50}Nb_{50}$ film thickness of 1300 Å. Bump height sensitivity is less than 10 Å for a one percent change in laser power. There is little variation in bump height sensitivity with film thickness as indicated in Table 1. Bump height sensitivity rises to greater than 20 Å for a one percent change in laser power for film thicknesses greater than 2000 Å.

Table 1. Bump height sensitivity at 150 to 200 Å bump height as a function of $Ni_{50}Nb_{50}$ film thickness. Laser pulse width is 65 ns.

Thickness (Å)	Sensitivity (Å / % laser power)
1000	3.4
1100	5.1
1200	6.5
1300	7.3
1500	6.6

To determine the uniformity of bump heights on a disk surface, 96 bumps on 12 tracks (two bumps in each of the four quadrants per track) were measured. The average bump height for this disk is 247 Å. The maximum and minimum bump heights are 263 Å and 214 Å. The standard deviation is 8.5 Å. These results are similar to those obtained on NiP/Al using the same laser tool.

To minimize stiction, it is desirable to reduce the bump diameter. Different compositions of Ni-Nb films were investigated. Alloy compositions with niobium content ranging from 16 to 60 atomic percent were studied. A plot of the bump width at the base of the bump as a function of niobium content is shown in Figure 4. There is a significant reduction in bump diameter for lower niobium content.

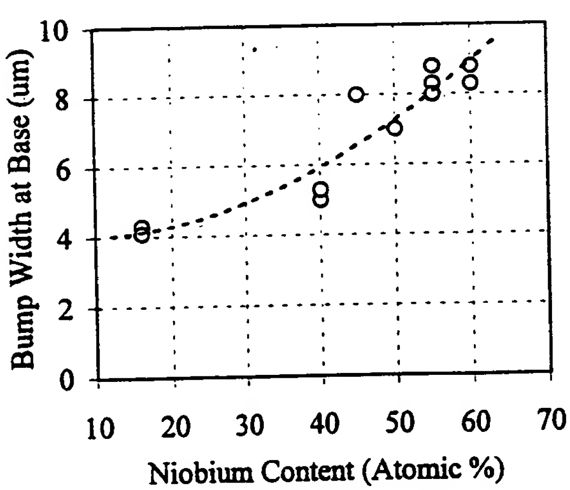

Figure 4. Bump width at base as a function of alloy composition. Bump heights are 400Å to 440Å for Nb content up to 50%. Maximum bump height is 245Å and 180Å for 55 at.% and 60 at.% Nb, respectively.

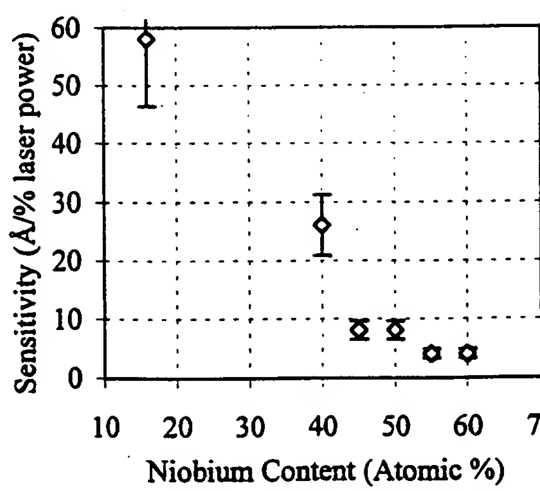

Figure 5. Bump height sensitivity as a function of alloy composition. Ni-Nb film thickness is 1300 Å. The slope of the bump height versus laser power curve is taken at a bump height of 150 - 200 Å. Laser pulse width is 65 ns.

The bump height sensitivity is also affected by niobium content. The plot in Figure 5 shows that the bump height sensitivity increases to unacceptable levels for niobium concentrations below 45 atomic percent.

Tribological performance of disks fabricated with laser texture of Ni-Nb on glass substrates is excellent. The result of 50,000 cycles of continuous start-stop testing using a conventional negative pressure slider is shown in Figure 6. Lube thickness is 36Å. Stiction values remain consistently low throughout.

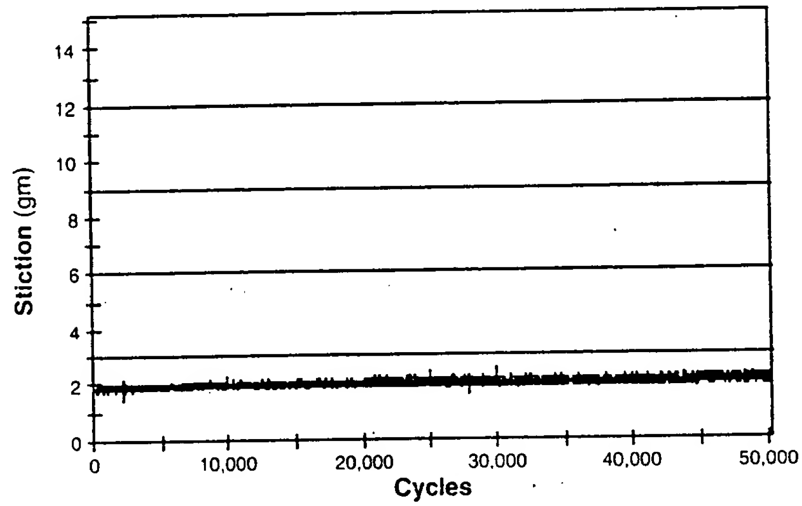

Figure 6. Continuous start-stop (CSS) test of finished disk with laser texture of $Ni_{50}Nb_{50}$ sputtered film. Bump height average is 170Å. Bump spacing is 60 µm circumferential and 30 µm radial.

Cross-section TEM, Figure 7, shows the Ni-Nb film to be smooth and featureless (no voids or columnar structure), consistent with a dense, amorphous film. The Ni-Nb film does not influence the properties or magnetic performance of the subsequently deposited CoCrPt film.

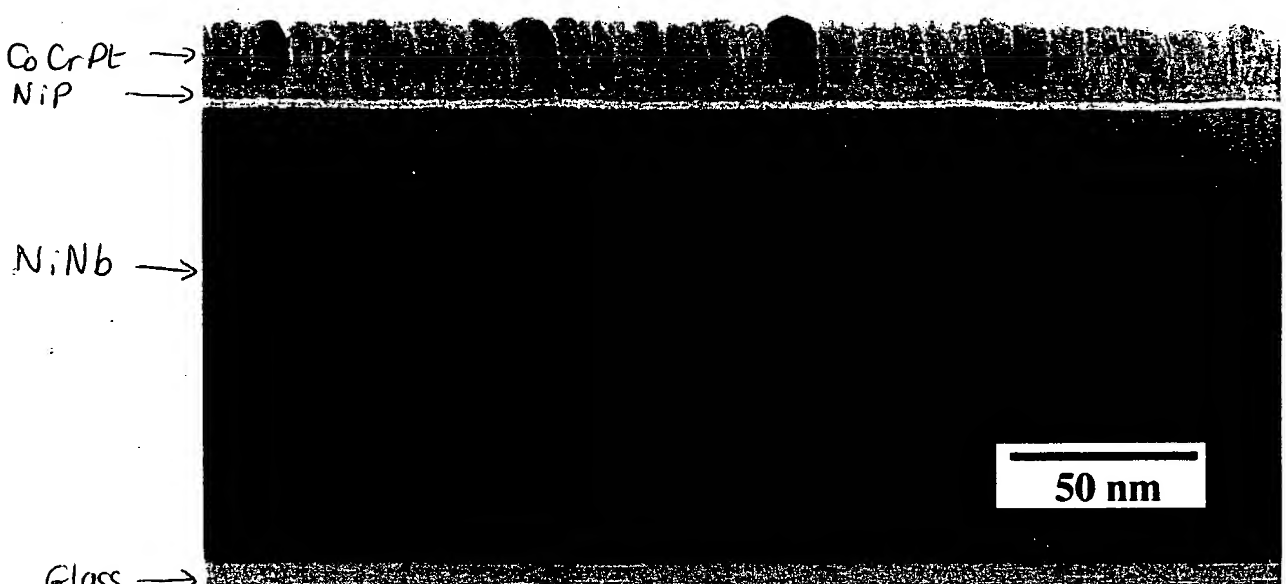

Figure 7. Cross-section TEM. Film structure: CoCrPt / NiP (sputtered) / Ni-Nb / glass

The exposure to atmosphere of the Ni-Nb layer for laser texture requires the use of a thin sputtered NiP layer deposited in-situ just prior to the CoCrPt. This provides for a fresh surface for improved nucleation of the magnetic layer.

CONCLUSION

A method has been developed which allows the use of conventional Q-switched infrared lasers to texture glass substrates. A sputtered thin film of nickel-niobium provides an absorption layer that generates regular, small conical shaped protrusions. Bump height sensitivity is in a range suitable for practical application, generating a narrow distribution of bump heights. Finished disks using this texture method exhibit excellent tribological performance. The texture layer has no influence on the subsequent deposition of the magnetic recording layer.

REFERENCES

1. B. Bhushan, Adv. Info. Storage Syst. **5**, 175 (1993).

2. R. Y. Ranjan, D. N. Lambeth, M. Tromel, P. Goglia, and Y. Li, J. Appl. Phys. **69**, 5745 (1991).

3. P. Baumgart, D. Krajnovich, T. Nguyen, and A. C. Tam, Data Storage 3, (3), 21-27 (1996).

4. T. W. Barbee, Jr., W. H. Holmes, D. L. Keith and M. K. Pyzyna, Thin Solid Films **45**, 591 (1977).

5. E. Teng, W. Goh and A. Eltoukhy, IEEE Transactions on Magnetics **32**, 3759 (1996).

6. T. D. Bennett, D. J. Krajnovich, C. P. Grigoropoulos, P. Baumgart and A. C. Tam, <u>ASME Proceedings of the 31st National Heat Transfer Conference</u>, HTD-323, 159-169 (1996).

Attachment B

Data provided from the specification of the pending application, Serial No. 09/559,347, showing the diffusion of Li from a glass substrate through to the top surface of a NiNb/CrMo/CoCrPtTa/carbon stack, wherein NiNb is used as a sealing layer.

Table I

NiNb thickness (Å)	CrMo/CoCrPtTa/carbon thickness (Å)	Li(counts/min)
0	630	2700
50	630	900
100	630	300
200	630	0